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Proposed Best Demonstrated Available Technology (BDAT) Background Document for Inorganic Pigment Wastes. Volume 1

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PROPOSED

BEST DEMONSTRATED AVAILABLE TECHNOLOGY (BDAT)

BACKGROUND DOCUMENT FOR

Inorganic Pigment Wastes

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1. INTRODUCTION

Pursuant to section 3004(m) of the Hazardous and Solid Waste Amendments (HSWA), enacted on November 8, 1984, the Environmental Protection Agency (EPA) is establishing treatment standards based on the best demonstrated available technology (BDAT) for inorganic pigment wastes. These wastes are identified in 40 CFR 261.32 as K002, K003, K004, K005, K006, K007, and K008. Compliance with these treatment standards is a prerequisite for placement of these wastes in facilities designated as land disposal units according to 40 CFR Part 268. The effective date of these treatment standards is May 6, 1990.

This background document presents the Agency's technical support and rationale for developing regulatory standards for these wastes. Sections 2 through 7 present waste-specific information for the K002, K003, K004, K005, K006, K007, and K008 wastes. Section 2 presents the number and location of facilities affected by the land disposal restrictions, the waste-generating process, and waste characterization data. Section 3 discusses the technologies used to treat the waste (or similar wastes), and Section 4 presents available performance data, including data on which treatment standards are based. Section 5 explains EPA's determination of BDAT, while Section 6 discusses the selection of constituents to be regulated. Proposed treatment standards are determined in Section 7.

The BDAT program and promulgated methodology are more thoroughly described in two additional documents: Methodology for Developing BDAT Treatment Standards (USEPA 1988c) and Generic Quality Assurance Project Plan for the Land Disposal Restrictions Program ("BDAT") (USEPA 1988b). The petition process to be followed in requesting a variance from the BDAT treatment standards is discussed in the methodology document.

It is EPA's understanding that three facilities presently generate K002, K003, and K006 (chrome pigment wastes) as defined. These wastes are the wastewater treatment sludges from the production of chrome inorganic pigments and for the purpose of BDAT are nonwastewaters. A wastewater is defined by the Agency as containing less than 1 percent (weight basis) total suspended solids* and less than 1 percent (weight basis) total organic carbon (TOC). Wastes not meeting this definition must comply with the treatment standards for nonwastewaters. Six facilities manufacture chrome inorganic pigments but do not generate a listed waste because they either recycle all process waters and solids or discharge the untreated wastewaters to publicly owned treatment works (POTWs). In addition, the Agency believes that the last company producing K005 and K007 ended production of the pigments from which these wastes were generated in June 1987. The Agency also believes, based on RCRA 3007 Questionnaire responses, that nonwastewater forms of K004 and K008 are not currently generated.

The proposed treatment standard for K002, K003, K004, K005, K006 (from anhydrous chrome oxide green production) K007, and K008 nonwastewaters is based on the use of chemical treatment, precipitation, and stabilization technologies in series for management of these wastes. The Agency proposes stabilization as the treatment standard for K006 nonwastewaters generated from the production of hydrated chrome oxide green pigment.

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* The term "total suspended solids" (TSS) clarifies EPA's previously used terminology of "total solids" and "filterable solids." Specifically, the quantity of total suspended solids is measured by Method 209c (Total Suspended Solids Dried at 103 to 105°C) in Standard Methods for the Examination of Water and Wastewater, 16th Edition (APHA, AWWA, and WPCF 1985).

The specific proposed BDAT treatment standards for K002, K003, K004, K005, K006 (from anhydrous chrome oxide green production), K007 and K008 non-wastewaters are shown in Table 1-1.

The specific proposed BDAT treatment standards for K006 non-wastewaters generated from the production of chrome oxide green is described in Table 1-2.

The proposed treatment standard for wastewater forms of K002, K003, K004, K005, K006, K007, and K008 is based on chemical reduction and precipitation. The specific treatment standards for these wastewaters are shown in Table 1-3.

Table 1-1 Proposed Treatment Standards for K002, K003, K004, K005, K006 (Anhydrous Chrome Oxide Green), K007 and K008 Nonwastewaters

Constituent	TCLP Concentration in mg/l
Chromium (total)	0.094
Lead (total)	0.37
Cyanide (K005 and K007 only)	Alkaline chlorination of the sludge or wastewater containing the sludge.

Table 1-2 Proposed Standards for K006 Generated from Production of Hydrated Chrome Oxide Green Nonwastewaters

Constituent	TCLP Concentration mg/l
Chromium (total)	5.2
Hexavalent Chromium	0.52

Table 1-3 Treatment Standards for K002, K003, K004, K005, K006, K007, and K008 Wastewaters

Constituent	Wastewater Concentration in mg/l	
	30 day average	24-hour maximum
Chromium (total)	1.2	2.9
Lead (total)	1.4	3.4
Cyanide (total) for K005 and K007 only	0.31	0.74

2. INDUSTRY AFFECTED AND WASTE CHARACTERIZATION

Wastes listed as K002, K003, K004, K005, K006, and K007 are generated as the wastewater treatment sludges from the production of inorganic pigments. Under 40 CFR 261.32 wastes identified as K002, K003, K004, K005, K006, and K007 are specifically listed as follows:

K002: Wastewater treatment sludge from the production of chrome yellow and orange pigments.

K003: Wastewater treatment sludge from the production of molybdate orange pigments.

K004: Wastewater treatment sludge from the production of zinc yellow pigment.

K005: Wastewater treatment sludge from the production of chrome green pigments.

K006: Wastewater treatment sludge from the production of chrome oxide green pigments (anhydrous and hydrated).

K007: Wastewater treatment sludge from the production of iron blue pigments.

The waste K008 is identified as oven residues from the production of chrome oxide green pigments. The Agency has determined that these listed wastes represent a single treatability group based on their similar physical and chemical characteristics. As described later in this section, EPA has examined the sources of the wastes, the specific similarities in the waste composition, applicable and demonstrated treatment technologies, and attainable treatment performance in order to support a simplified regulatory approach for these inorganic wastes.

2.1 Industry Affected and Process Description

The four-digit Standard Industrial Classification (SIC) code associated with the production of inorganic pigments is 2816. These pigments are used extensively in paints, printing ink, floor covering

products, and paper. In addition, they may also be used in ceramics, cement, and asphalt roofing.

The Agency believes that two facilities generate both K002 and K003, and two facilities generate K006. It is the Agency's understanding that one chrome oxide green manufacturing facility which generates a K006 waste produces only hydrated chrome oxide green; anhydrous chrome oxide green is manufactured at the second facility, which recycles all wastes.* Based on available information, the Agency also believes that the last company in the United States to generate K005 and K007 ended production in June 1987. Table 2-1 lists the names and locations of the current known generators of K002, K003, and K006; the treatment and disposal methods used at these facilities; and the approximate product production levels achieved.

The Agency also identified those facilities that manufacture inorganic pigments but do not generate wastewater treatment sludges. These six facilities either discharge their untreated wastewaters to an NPDES regulated system (i.e., exempted from RCRA regulations) or recycle their solids by blending them with product for subsequent sale. Table 2-2 identifies these facilities.

Below are descriptions of the five pigment manufacturing processes that EPA identified as generating K002, K003, K004, K005, K006, and K007.

K002 - *Wastewater treatment sludges from the production of chrome yellow and orange pigments*

Chrome yellow and orange pigments (lead chromate) are produced by reacting sodium dichromate, caustic soda, and lead nitrate as follows. First, lead oxide or elemental lead is dissolved in nitric acid to

---

* Neither facility generates any K008 wastes.

Table 2-1 Present Chrome Pigments Manufacturers That Generate K002, K003, and K006 Wastes

Plant	Location	Products Manufactured			Total product production volumes	Wastes generated
		Chrome yellow	Molybdate orange	Chrome oxide green		
Pfizer	Lehigh Gap, PA			X(2)	B	K006
Harshaw Filtrol	Louisville, KY	X(2)	X(2)		A	K002, K003
Heubach	Newark, NJ	X(1)	X(1)		A	K002, K003

(1) Listed waste generated and sold for feedstock to lead smelter.
(2) Listed waste generated and land disposed offsite.

Reference: 3007 Questionnaire responses and telephone conversations with facilities to clarify responses (10/87 - 1/88).

A = >5,000 TPY
B = <5,000 TPY

Table 2-2 Chrome Pigment Manufacturers That Recycle Wastes or Wastewaters or Discharge Untreated Wastewaters to POTW Systems

Plant	Location	Chrome yellow and orange	Molybdate orange	Chrome oxide green	Zinc yellow	Reason for no waste generation
NJZ Colors	Brooklyn, NY	X	X			Discharge to POTW
KiKuchi Color	Patterson, NJ	X				Discharge to POTW
American Chrome and Chemical	Corpus Christi, TX			X		Total reuse of waste generated
NL Chemicals	St. Louis, MO	X				Total process water recycle
Wayne Pigments	Milwaukee, WI	X	X		X	Discharge to POTW
Mineral Pigments	Beltsville, MD				X	Consumptive use of wastewater to produce a byproduct

Reference: 3007 Questionnaire responses and telephone conversations with facilities to clarify responses (10/87 - 1/88).

generate a lead nitrate solution. This solution is then mixed with an alkaline solution of sodium dichromate. The reaction that occurs may be written as follows:

$$Na_2Cr_2O_7 + 2NaOH + 2Pb(NO_3)_2 \rightarrow 2PbCrO_4 + 4NaNO_3 + H_2O.$$

Lead chromate (a hexavalent species) is formed as a precipitate and is recovered by filtration, then washed, dried, milled, and packaged. The filtrate and wash waters, containing lead and hexavalent chromium compounds, are sent to a wastewater treatment facility. Figure 2-1 presents a general schematic of a typical lead chromate production and waste treatment process.

K003 - *Wastewater treatment sludges from the production of molybdate orange pigments*

Molybdate orange pigment is made by the coprecipitation of lead chromate ($PbCrO_4$) and lead molybdate ($PbMoO_4$). Molybdic oxide is first dissolved in aqueous sodium hydroxide, then sodium chromate is added. This solution is mixed with a solution of lead oxide in nitric acid. The product, a mixture of lead chromate and lead molybdate, precipitates from solution.

The precipitate (lead chromate and lead molybdate) is collected by filtration, then washed, dried, milled, and packaged. The filtrate contains unreacted sodium chromate and sodium molybdate, lead ions, and some suspended particulates of unrecovered products. This wastewater stream is usually sent to a wastewater treatment facility. The wastewater treatment sludge produced is the listed waste K003. Figure 2-2 presents a general schematic of a typical molybdate orange production and waste treatment process.

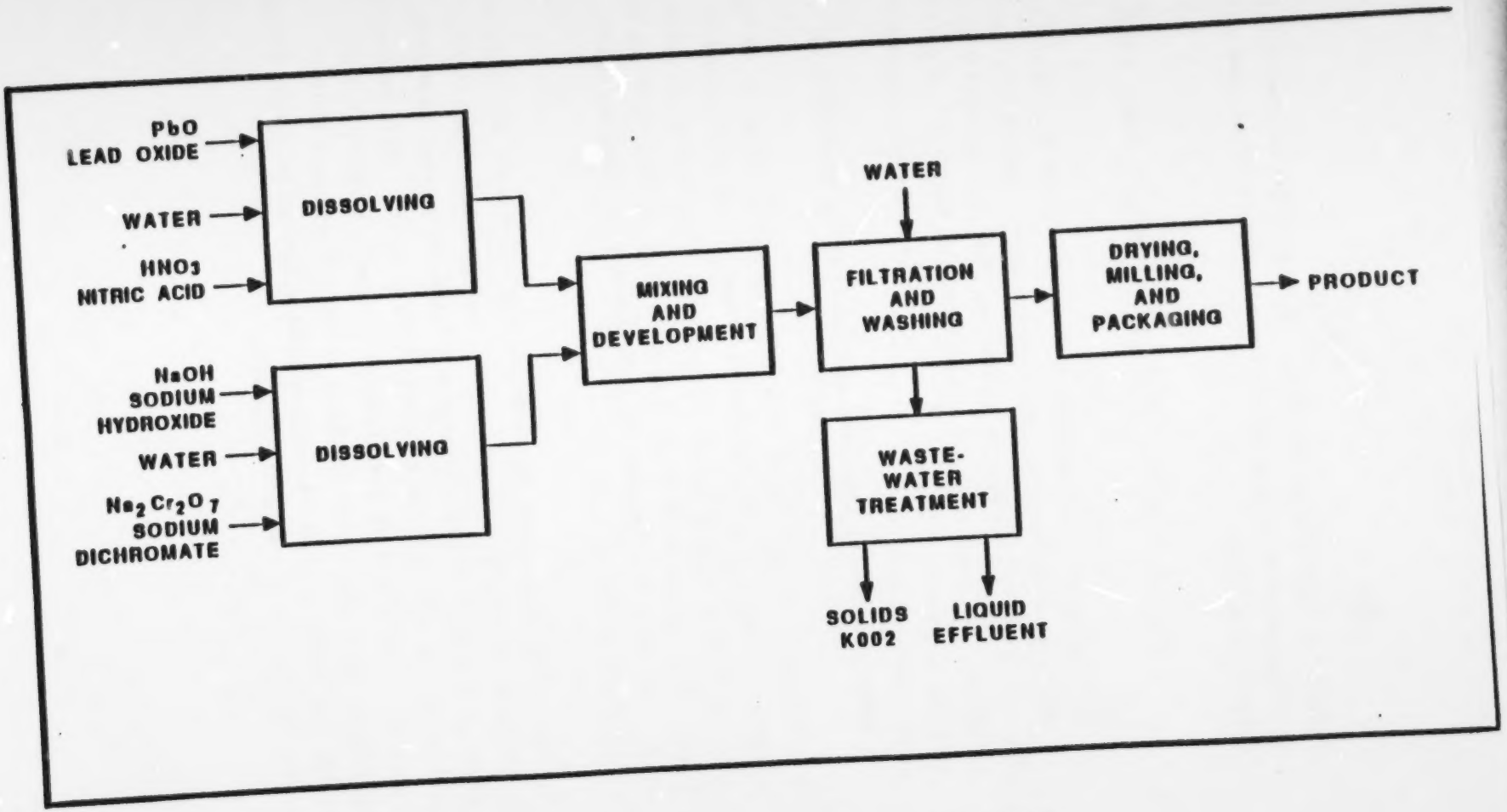

FIGURE 2-1 CHROME YELLOW MANUFACTURE

K004 - *Wastewater treatment sludges from the production of zinc yellow pigments*

Zinc yellow pigments are produced by two processes. In the first process chromic acid solution is reacted with zinc oxide or zinc carbonate. The product precipitates from solution and is collected by filtration, then washed, dried, and packaged. The spent process liquor and wastewaters are combined and forwarded to a second process, where barium carbonate is added. Barium chromate now precipitates, is collected by filtration, and then is washed, dried, and packaged. The spent process and wash waters from these operations are combined and used to prepare the chromic acid solutions for the zinc yellow process at the one facility using this process. Figure 2-3 shows a diagram of the process.

The second process for zinc yellow products involves reaction of a solution of potassium dichromate with an added zinc salt, such as the nitrate or chloride. The product precipitates from solution. The reaction equation is:

$$2K_2Cr_2O_7 + 4ZnCl_2 + 6H_2O \text{ --->}$$

$$4ZnO \bullet K_2O \bullet 4CrO_3 \bullet 3H_2O \text{ (zinc yellow)} + 2KCl + 6HCl.$$

The precipitate is then collected by filtration, washed, dried, and packaged. The spent process liquors and wash waters are combined and released to a local POTW at the one facility using the process. Figure 2-4 shows the process diagram.

K005 - *Wastewater treatment sludges from the production of chrome green pigments*

Chrome green pigments are no longer manufactured in the United States. These pigments are mixtures of chrome yellow and iron blue (iron

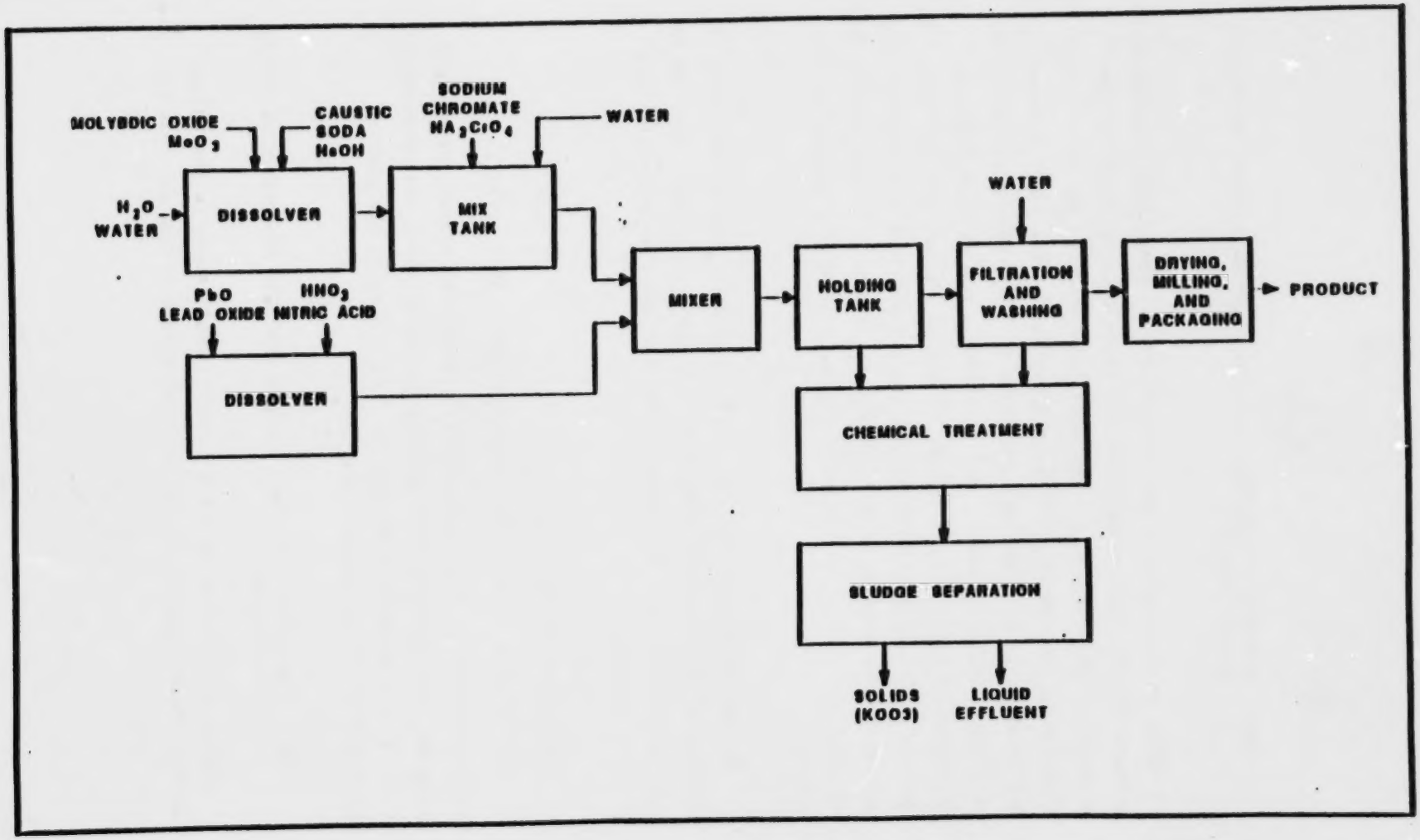

FIGURE 2-2 MOLYBDATE ORANGE MANUFACTURE

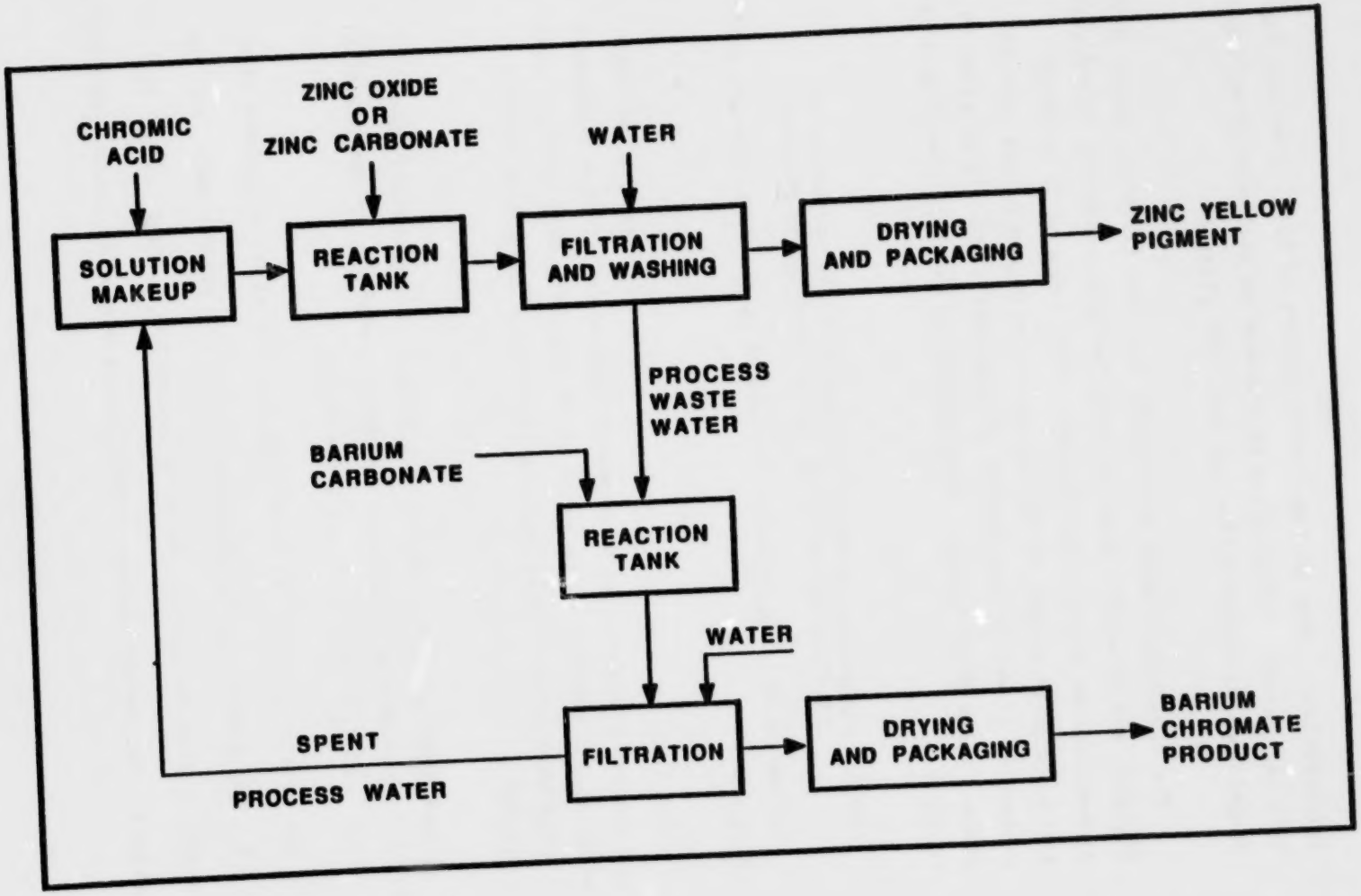

FIGURE 2-3 ZINC YELLOW PIGMENT MANUFACTURE BY THE MINERAL PIGMENTS PROCESS

ferrocyanide). They include a wide variety of hues, from very light to very dark green. Chrome green is produced by mechanically mixing aqueous dispersions of chrome yellow and iron blue pigments.

The resulting pigment suspensions are then filtered, dried, ground, blended, and packaged. When the sole facility producing chrome green pigment was operating, the filtrate, which contains unrecovered particulates of chrome yellow and iron blue pigments, was sent to wastewater treatment for removal of suspended particulates prior to release under NPDES permit. This production facility closed permanently in 1987.

K006 - *Wastewater treatment sludges from the production of anhydrous and hydrated chrome oxide green pigments*

Chrome oxide green pigment is produced at two facilities by different processes.

The first process, which produces anhydrous chromic oxide, employs the thermal decomposition of ammonium dichromate. Sodium dichromate solution and ammonium sulfate are mixed together; this mixing results in a solid mass consisting of ammonium dichromate and sodium sulfate decanydrate ($Na_2SO_4 \cdot 10H_2O$).

This mixture is then heated in a kiln to a temperature above 500°C. The ammonium dichromate decomposes according to the reaction:

(a) $(NH_4)_2\ Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O$.

The reacted material is recovered from the kiln and leached with water. The sodium sulfate dissolves out of the product mass, and the leached product is then recovered by filtration, washed, dried, and packaged. The sodium sulfate-containing wastewater is treated to reduce

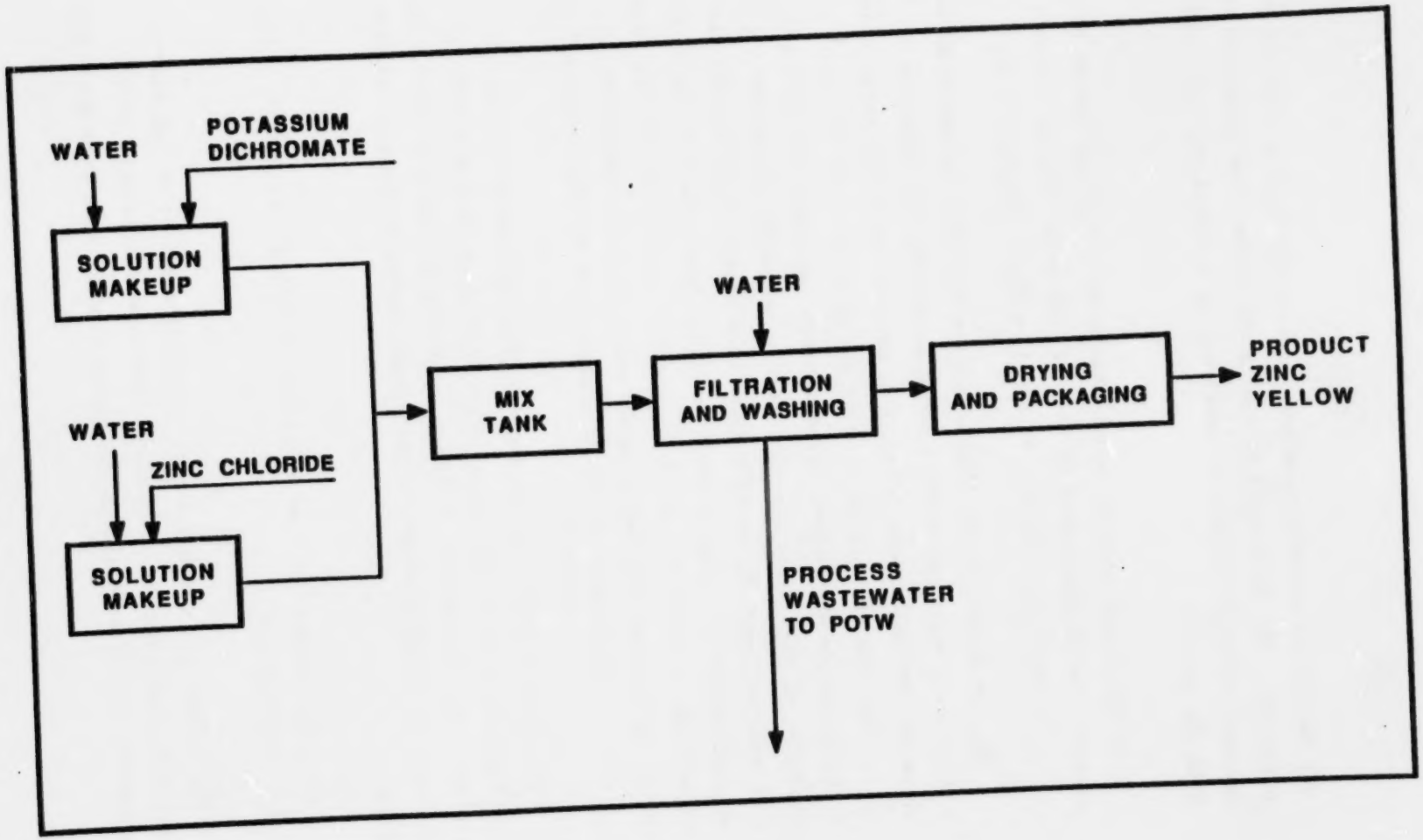

FIGURE 2-4 ZINC YELLOW PRODUCTION BY THE WAYNE PIGMENTS PROCESS

any hexavalent chromium compounds present and then is filtered prior to discharge. The K006 waste stream is the filter cake generated from this process, which is collected, reclaimed in a second calciner, and blended with the product.

In the second process, which manufactures hydrated chrome oxide green pigment, sodium dichromate is reacted with boric acid as follows:

$$2Na_2Cr_2O_7 + 8H_3BO_3 \rightarrow 2Cr_2O_3 \cdot 2H_2O + 2Na_2B_4O_7 + 8O_2.$$

The raw materials are blended in a mixer, then heated in an oven at 550°C. Oven residues, which contain hexavalent and trivalent chromium, are washed out of the oven and sent to a wastewater treatment unit. The reacted material is slurried with water and filtered. The filtered solids are washed, dried, ground, screened, and packaged. The filtrate and wash water are also sent to wastewater treatment where chemical treatment of the wastewater with sodium bisulfite and lime neutralization in series followed by filtration generates the listed waste K006. Figures 2-5 and 2-6 present schematics of the two types of chrome oxide green manufacturing and waste treatment processes.

K007 - *Wastewater treatment sludges from the production of iron blue pigments*

Iron blue pigments are produced by the reaction of sodium ferrocyanide with an aqueous solution of iron sulfate and ammonium sulfate. The precipitate formed is separated and oxidized with sodium chlorate or sodium chromate, a hexavalent chromium compound, to form iron blues.

The final product is then collected by filtration, washed, dried, milled, and packaged.

The wastewaters contain all of the chemicals used in the process, along with some unrecovered product. Subsequent treatment of the wastewaters generates a sludge containing complex iron cyanides. EPA

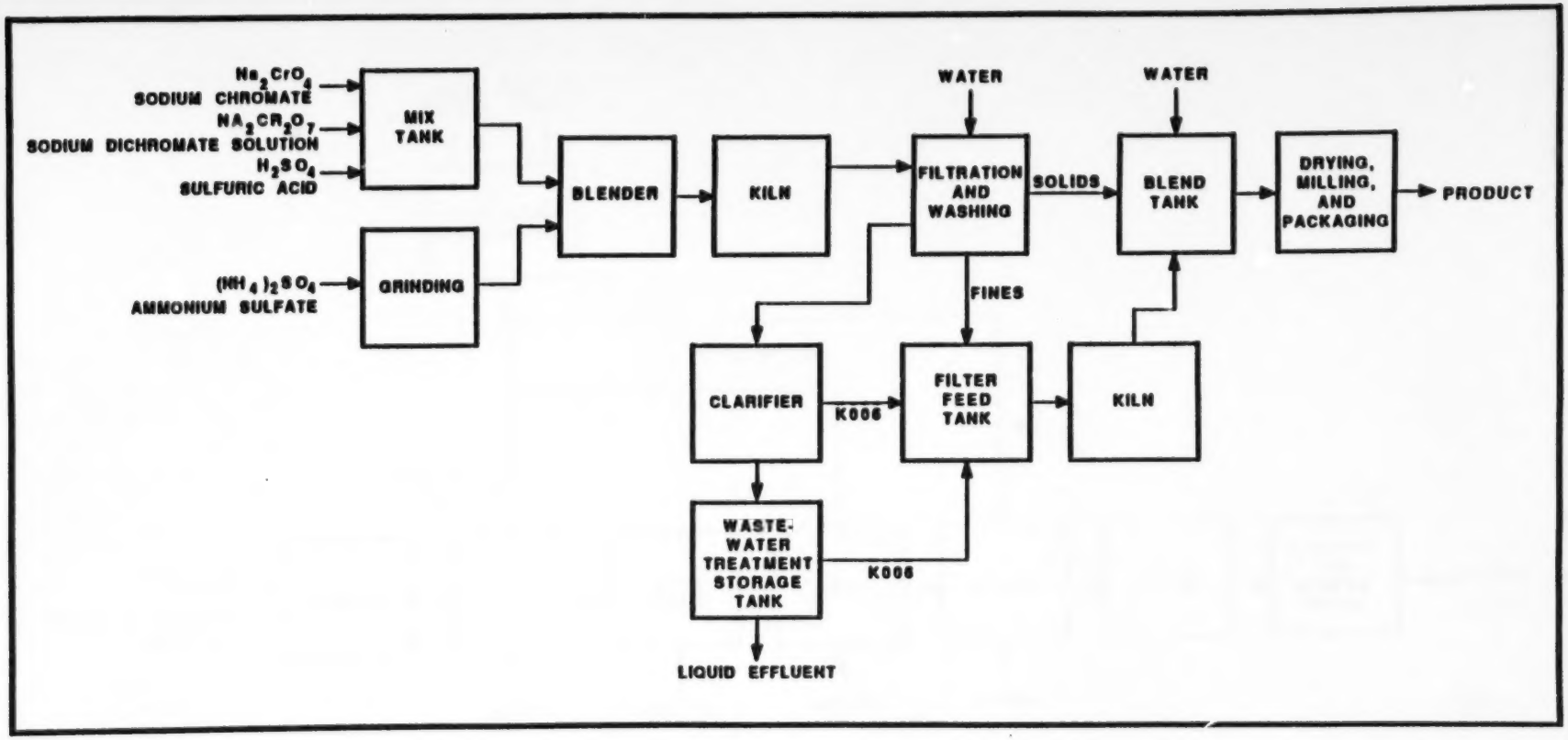

FIGURE 2-5 HYDRATED CHROME OXIDE GREEN MANUFACTURE BY THE AMMONIUM DICHROMATE PROCESS

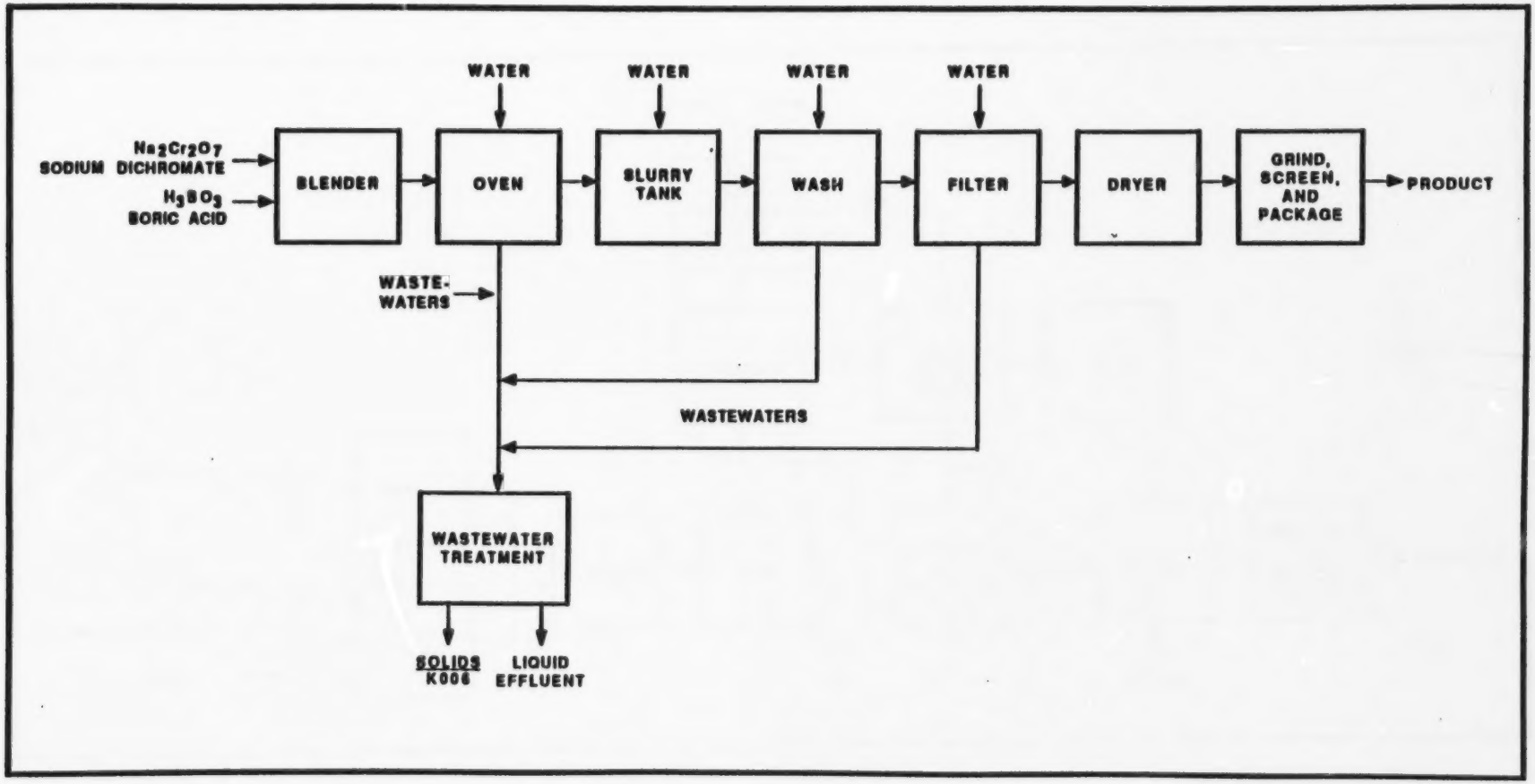

FIGURE 2-6 HYDRATED CHROME OXIDE GREEN MANUFACTURE BY THE BORIC ACID PROCESS

believes that the last facility producing iron blues in the United States closed permanently in June 1987.

K008- *Oven cleanout residues from the production of chrome oxide green pigments*

The two processes described previously as the sources of generation of K006 waste are the potential generators of K008 wastes if the reaction kiln or oven is cleaned by dry methods. Presently, both K006 generation facilities employ wet cleaning methods. The wastewater generated is combined with other process wastewaters prior to treatment. The wastewater treatment sludges generated as a result of this waste treatment become K006. They contain all of the chromium values which would have been removed from the kiln or oven as dry solids had dry cleanout methods been used.

2.2 Waste Characterization

Waste characterization data for waste codes K002, K003, K004, K005, K006, K007, and K008 that were available to the Agency are summarized below. Table 2-3 contains specific characterization data for waste codes K002, K003, and K004 from an onsite engineering study. The wastewater treatment processes responsible for generation of these sludges did not include any hexavalent chromium reduction steps so that chromate salts are present in the wastes from this one facility. Table 2-4 contains waste characterization data obtained by the Agency for a second plant generating a mixed K002/K003 wastewater treatment sludge. These results show the wastes produced at the facility are highly variable. Table 2-5 shows waste characterization data for the K006 waste generated from the one facility producing hydrated chrome oxide green. Table 2-6 presents estimated general data for the major contaminants in wastes K002, K003, K004, K005, K006, K007, and K008 along with their approximate concentrations from the original listing documents. Only very limited

Table 2-3 BDAT Metals Concentrations for the Chromate and Carbonate Sludge Samples

BDAT constituent (ppm)	K002/K003 Yellow chromate sludge	Mixture of K002, K003, and K004 Carbonate sludge	K002/K003 Orange chromate sludge
Antimony	ND	ND	ND
Arsenic	ND	ND	ND
Barium	530	ND	700
Beryllium	ND	ND	ND
Cadmium	ND	ND	ND
Chromium (T)	108,000	850	74,000
Copper	ND	ND	ND
Lead	670,000	750,000	610,000
Mercury	0.27	ND	ND
Nickel	ND	ND	ND
Selenium	ND	ND	ND
Silver	ND	ND	ND
Thallium	ND	ND	ND
Vanadium	ND	ND	ND
Zinc	290	85,000	710
Total cyanide	ND	ND	ND
Sulfide	NA	NA	ND
Other constituents	balance	balance	balance

ND = Not detected.
NA = Not analyzed.

Reference: USEPA 1987.

Table 2-4 Waste Characterization Data for a Mixed K002/K003 Waste Generated at a Chrome Pigments Production Facility

Constituent	Total Composition[1] (ppm) Sample 1	Sample 2	EP Toxicity Leachate (ppm) Sample 1	Sample 2	Sample 3	Sample 4
Cadmium[2]	1,476	-	18	0.98	3.75	3.81
Chromium	61,800	-	13	<.01	<0.1	<0.1
Lead	54,700	-	64.5	<.01	308	150
Zinc	2,400	-	-	-	-	-
Barium	1,093	-	-	-	-	-
Water	393,000	-	-	-	-	-
Total Solids	607,000	602,000	-	-	-	-

[1]Sample 1 was obtained on April 25, 1988 and Sample 2 was obtained on March 3, 1989. Samples 3 and 4 were obtained on unspecified dates in August and September, 1988 respectively.

[2]The source of the cadmium is another process unrelated to chrome pigments production.

Source: Engelhard, 1989.

Table 2-5 Waste Characterization Data for K006 Waste Generated from Facility Producing Hydrated Chrome Oxide Green Pigment

Constituent	Concentration dry weight basis
Arsenic	<2.0 ppm
Barium	<20 ppm
Cadmium	<0.6 ppm
Chromium	81,000 ppm
Lead	9.7 ppm
Mercury	<0.6 ppm
Selenium	<2.0 ppm
Silver	<0.6 ppm

Source: Pfizer Inc., communication to EPA, June 22, 1989.

Table 2-6 Estimated Composition of Wastewater Treatment Sludges from Inorganic Pigments Manufacturing Processes

Sludge source	Estimated contaminants in sludge
K002 Production of chrome yellow and orange pigments	30,000 ppm $PbCrO_4$ lead chromate 10,400 ppm $Cr(OH)_3$ chromium hydroxide 2,500 ppm $Pb(OH)_2$ lead hydroxide
K003 Production of molybdate orange pigments	20,000 ppm $PbCrO_4$ -$PbMoO_4$ (molybdate orange) 10,000 ppm $(Cr(OH)_3$ chromium hydroxide 2,500 ppm $Pb(OH)_2$ lead hydroxide
K004 Production of zinc yellow pigments	20,000 zinc yellow pigment 48,000 chromic hydroxide
K005 Production of chrome green pigments	5,000 ppm $PbCrO_4Fe$ $(NH_4)[Fe(CN)_6]$
K006 Production of anhydrous chrome oxide green pigments	22,000 ppm $Cr(OH)_3$ chromium hydroxide
K006 Production of hydrated chrome oxide green pigments	66,000 ppm $Cr(OH)_3$ chromium hydroxide
K007 Production of iron blue pigments	25,000 ppm $Fe_4(Fe(CN)_6)_3$ ferric ferrocyanide
K008 Production of chrome oxide green pigments	10,000 chromium oxides

Reference: USEPA 1980a.

data are presently available for characterization of wastewater forms of K002, K003, K004, K005, K006, K007, or K008. These wastewaters would consist of leachates from landfills containing these pigment wastes or filtrates from dewatering nonwastewater sludges.

2.3 Determination of Waste Treatability Group

In some cases EPA believes that wastes with different waste codes produced in similar processes in an industry or in similar industries, can be treated to similar concentrations by using the same technologies. In these instances, the Agency may combine the codes into a single treatability group. Based on careful review of the generators of inorganic pigments and available waste characterization data, the Agency has determined that wastes K002, K003, K004, K005, K006, K007 and K008 represent a single treatability group. The concentration and type of metal constituents in the various wastes are dependent upon the waste type, the particular production process employed, and the specifics of the treatment process. However, all the wastes contain similar constituents and are expected to be treatable to similar levels by using the same technology for metals. The same complex cyanides are present in two of the wastes, K005 and K007, and are treatable by the same processes.

With respect to wastes K005 and K007, EPA has determined that the pigments from which these wastes were generated are no longer produced in the United States. However, some firms could wish to produce these pigments again at some future date.

Process changes occurring in the last decade have eliminated the generation of K008 non-wastewaters from the manufacture of both hydrated and anhydrous chrome oxide green pigments. Dry cleaning of ovens and kilns has been eliminated. Presently, washout waters from oven or kiln cleaning are combined with other chrome oxide green process wastewaters

and treated to generate a K006 waste at the two facilities manufacturing chrome oxide green pigments. However, it is possible that in the future the old waste management methods will be resumed and, there are significant quantities of these wasates presently in existence.

Wastewater treatment sludges from the production of zinc yellow pigment (K004) are not generated at either of the two facilities producing this product. One facility sends its untreated wastewater to a POTW for treatment. The second plant uses a new process chemistry and is able to recycle all wastewater and generates a co-product barium chromate pigment for sale. Both of these wastewater management methods could change in future years due to changes in POTW regulations and demand for barium chromate.

The wastewater forms of K002, K003, K004, K005, K006, K007, and K008 constitute a single treatability group because of the similarity of their constituents. These wastes consist of leachates from landfills containing these wastes or filtrates from dewatering non-wastewater forms of these wastes. Most chrome pigment and iron blue production facilities historically manufactured a wide variety of inorganic pigments, with the result that their landfills are likely to contain mixed wastes from a number of individual production processes.

3. APPLICABLE AND DEMONSTRATED TREATMENT TECHNOLOGIES

Section 2 established a single treatability group for the management of K002, K003, K004, K005, K006, K007 and K008 wastes. This section identifies the treatment technologies that are applicable to this group and determines which, if any, of the applicable technologies can be considered demonstrated for the purpose of establishing BDAT.

To be applicable, a technology must be theoretically usable to treat the waste in question or to treat a waste that is similar in terms of the parameters that affect treatment selection. (For detailed descriptions of the technologies applicable for these wastes, or for wastes judged to be similar, see EPA's Treatment Technology Background Document (USEPA 1988d).) To be demonstrated, the technology must be employed in full-scale operation for the treatment of the waste in question or a similar waste. Technologies available only at pilot- and bench-scale operations are not considered in identifying demonstrated technologies.

3.1 Applicable Treatment Technologies

3.1.1 Treatment Technologies for Nonwastewaters

Initial data gathering on the treatment of these wastes included review of the technical literature, review of RCRA 3007 Questionnaires, and contacts with industry representatives. As a result of these efforts, EPA has identified three technologies as potentially applicable for treatment of these wastes. These technologies are stabilization, high temperature metals recovery (HTMR), and reuse/recycle.

With respect to nonwastewaters, stabilization reduces the leachability of the metals, HTMR reduces both the total concentration and the leachability of the metals through the production of slag, and product reuse/recycle eliminates the waste stream entirely.

The Agency believes that stabilization with prior chemical treatment can be used to treat these wastes; this belief is based on the chemical and physical similarity of these wastes to F006 (wastewater treatment sludges from electroplating operations) and also the similarity of the untreated pigment production wastewaters to the waste K062 (waste pickle liquor). Also, the Agency is of the opinion that HTMR can be used to treat K002, K003, and K006 because of the chemical and physical similarities of these wastes to K061 (electric arc furnace dust); all are solid wastes with a high metal content.

Stabilization and high temperature metals recovery are discussed fully in the F006 Background Document (USEPA 1988a) and in the Treatment Technology Background Document (USEPA 1988d). Product reuse/recycle involves the elimination of the nonwastewater streams by reuse in the manufacture of another product or recycle of all nonwastewater process residuals in the production cycle.

The Agency believes that the wastes K004 and K008 are similar to K002, K003, and K006 with respect to concentrations of specific toxic metals present both because K004 and K008 contain comparable concentrations of chromates. Therefore K004 and K008 nonwastewaters can be managed by the same technologies as K002, K003, K004 and K006. The Agency also believes that the wastes K005 and K007, which will contain complex cyanides are manageable by the same technologies used to treat the wastes F006 and F007 because these F006 and F007 wastes contain comparable forms and higher concentrations of cyanides and hence should be more difficult to treat than the K005 and K007 wastes.

3.1.2 Treatment Technologies for Wastewaters

Wastewater forms of K002, K003, K004, K005, K006, K007, and K008 consist primarily of leachates from landfills into which these wastes

were deposited and filtrates from dewatering of waste sludges. All of these wastes were originally generated by treatment of process wastewaters from the production of the chrome and iron blue colors. As a result, the leachates are expected to contain those constituents originally removed from the wastewaters [i.e., chromium, lead, and complex cyanides). The treatments, first discussed in the Development Document for Effluent Limitations Guidelines (i.e., Best Available Technology Economically Achievable (BATEA)], New Source Performance Standards and Pretreatment Standards for the Inorganic Chemicals Manufacturing Point Source Category (USEPA 1981), were chemical reduction and hydroxide and lime precipitation. These technologies are also discussed in more detail in the Treatment Technology Background Document (USEPA 1988d).

3.2 Demonstrated Treatment Technologies

3.2.1 Demonstrated Technologies for Nonwastewaters

Of the above-mentioned applicable technologies, all have been demonstrated on the pigment production wastes or similar wastes. Chemical reduction and stabilization have been demonstrated on F006 wastes (wastewater treatment sludges from electroplating operations) and on K061 wastes (electric arc furnace dust), and HTMR has been demonstrated on K061, which, as previously mentioned, is also similar to K002, K003, and K006. Chemical reduction has also been demonstrated on K062 waste pickle liquor from iron and steel manufacturing. In addition, stabilization data have been provided to the Agency by the sole generator of K006 wastes generated by the production of hydrated chrome oxide green pigments. The Agency has identified a facility that is practicing product reuse and recycle, in conjunction with HTMR, for a mixed K002/K003 waste, and also has stabilization data for this waste. In addition, the Agency is aware of a facility that recycles its solids (K006) resulting from the manufacture of anhydrous chrome oxide green.

Product reuse/recycle of mixed K002/K003 involves the addition of lead salts to the process wastewater; the lead salts act as a precipitating agent and raise the lead content of the sludge. The sludge is subsequently sold to a lead smelter to be used as a feedstock substitute for the smelter's raw material (lead-bearing scrap materials). This sludge consists primarily of lead chromate and lead carbonate, which occur in nature as the lead bearing minerals crocoite and cerussite, respectively.

According to information supplied to the Agency, the recycle of K006 nonwastewaters from production of anhydrous chrome oxide green pigment results in the reduction of BDAT metals in the wastewater residuals generated from the production of chrome oxide green. Solids from the wastewater treatment system are recycled back to the production process for inclusion in the finished product. The solids are chemically identical to the product chrome oxide green.

The Agency however believes these reuse/recycle technologies may be plant and product grade specific and hence not applicable to all potential generators of K006 nonwastewaters. The Agency also acknowledges that reuse and recycle are demonstrated for some K002 and K003 nonwastewaters but also feels these technologies may only be applicable only under certain specialized conditions. The Agency also notes that processing of the wastes at lead smelters may generate residues requiring treatment and disposal. For K006 originating from the production of hydrated chrome oxide green, it appears that these wastes because of their low chromium content, may not be easily recycled. Therefore, based on analysis of data available on the stabilized K006 waste from this source, stabilization is a treatment technology which is applicable in this case.

K002 and K003 wastes will vary in their TCLP toxic metal content depending on the wastewater treatment methods used. Two facilities presently generate mixed K002 and K003 wastes. One facility generates a sludge containing lead chromate and lead carbonate which it then sells to a lead smelter. This is the waste whose composition was given in Table 2-3. The second facility treats its wastewater with ferrous sulfate and lime in series to generate a waste containing considerable amounts of iron oxides and hydroxide, trivalent chromium hydroxide, and sparingly soluble lead salts, which has much lower lead content. As recycle of this waste may be problematic, the Agency considers that chemical treatment and stabilization in series is an applicable treatment train for this type of K002 and K003 waste.

The Agency would still prefer the use of a technology that recycles the toxic metals of concern, but is unable to require it at this time due to the potential problems previously discussed.

3.2.2 Demonstrated Technologies for Wastewater

The use of chromate reduction cyanide oxidation and chemical precipitation technologies by the inorganic pigments industry are discussed in detail in the Development Document for Effluent Limitations Guidelines, New Source Performance Standards and Pretreatment Standards for the Inorganic Chemicals Manufacturing Point Source Category (USEPA 1982). Extensive documentation is presented on the use of these technologies by the pigments industry and on the results normally obtained with these technologies.

4. PERFORMANCE DATA BASE

This section presents the data available to EPA on the performance of demonstrated technologies in treating the listed wastes. These data are used elsewhere in this document for determining which technologies represent BDAT (Section 5), for selecting constituents to be regulated (Section 6), and for developing treatment standards (Section 7). Eligible data, in addition to full-scale demonstration data, may include data developed at research facilities or obtained through other applications at less than full-scale operation, as long as the technology is demonstrated in full-scale operation for a similar waste or wastes as defined in Section 3.

Performance data, to the extent that they are available to EPA, include the untreated and treated waste concentrations for a given constituent, values of operating parameters for the treatment technology that were measured at the time the waste was being treated, the values of relevant design parameters for the treatment technology, and data on waste characteristics that affect performance of the treatment technology.

Where data are not available on the treatment of the specific wastes of concern, the Agency may elect to transfer data on the treatment of a similar waste or wastes, using a demonstrated technology. To transfer data from another waste category, EPA must find that the wastes covered by this background document are no more difficult to treat (based on the waste characteristics that affect performance of the demonstrated treatment technology) than the treated wastes from which performance data are being transferred.

The Agency has stabilization data for a mixed untreated and treated K002/K003/K004 waste generated from a wastewater treatment system that

does not utilize hexavalent chromium reduction.* This waste was obtained from a facility that produced chrome yellow, molybdate orange, and zinc yellow pigments in 1985 and 1986. The facility phased out production of zinc yellow in early 1987, but still produces the other two pigments. The untreated leachate data are presented in Table 4-1 and the treated leachate data are presented in Table 4-2. The Agency also has received data from the one facility producing hydrated chrome oxide green pigment. Table 4-3 shows the results of TCLP tests conducted on five samples of stabilized K006 wastes from the one facility.

The Agency does not have data on stabilization of the K002/K003 wastes generated from the facility using ferrous sulfate treatment of its process wastewaters. However, the Agency expects that this waste will behave similar to both F006 and treated K062 wastes with respect to stabilization because the same constituents are present at comparable levels. Data on stabilization of F006 wastes is in the F006 Background Document (USEPA 1988a). Data on the treatment and subsequent lime stabilization of K062 wastes is presented in the K062 background document (USEPA 1988f). With respect to reuse/recycle, the Agency has documentation from three facilities recycling K002, K003, and/or K006 nonwastewaters and has noted the special circumstances accompanying use of these technologies.

The Agency also has a considerable amount of wastewater treatment data, applicable to wastewater forms of K002, K003, K004, K005, K006, K007, and K008 which is presented in the Development Document for

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*Use of chromate reduction technologies will convert any chromates present to trivalent chromium hydroxide. Chromates are generally soluble. Trivalent chromium hydroxide, however, is essentially insoluble, and thus more easily managed by stabilization.

Table 4-1 BDAT TCLP Metal Values for Untreated Inorganic Pigment Sludges

BDAT constituent	K002/K003 Yellow chromate sludge (ppm)	K002/K003/K004 Carbonate sludge (ppm)	K002/K003 Orange chromate sludge (ppm)
Arsenic	ND	ND	ND
Barium	ND	0.09	ND
Cadmium	ND	0.047	ND
Chromium (TOT)	1.2	1.3	2.7
Lead	320	5400	1600
Mercury	ND	ND	ND
Selenium	ND	ND	ND
Silver	ND	ND	ND

ND = None detected at practical quantitation limit.

Reference: USEPA 1987.

Table 4-2 TCLP Analytical Results for the Treated (Stabilized) Combined Wastewater Treatment Sludge Samples K002/K003/K004

	Treated waste (cement binder) TCLP sample number		
	A mg/l	B mg/l	C mg/l
Antimony	ND	ND	ND
Arsenic	ND	ND	ND
Barium	0.2	0.26	0.47
Beryllium	ND	ND	ND
Cadmium	ND	ND	ND
Chromium (Total)	9.9	1.9	ND
Copper	ND	ND	ND
Lead	0.13	0.16	1.34
Mercury	ND	ND	ND
Nickel	ND	ND	ND
Selenium	ND	ND	ND
Silver	ND	ND	ND
Thallium	ND	ND	ND
Vanadium	ND	ND	ND
Zinc	0.094	0.24	ND
	Kiln dust binder		
Antimony	ND	ND	ND
Arsenic	ND	ND	ND
Barium	0.088	0.024	0.18
Beryllium	ND	ND	ND
Cadmium	ND	ND	ND
Chromium (Total)	39.1	1.6	ND
Copper	ND	ND	ND
Lead	6.6	13.5	1.5
Mercury	ND	ND	ND
Nickel	ND	ND	ND
Selenium	ND	ND	ND
Silver	ND	ND	ND
Thallium	ND	ND	ND
Vanadium	ND	ND	ND
Zinc	2.3	1.7	ND

A = 84% K002/K003, 16% K002/K003/K004
B = 84% K002/K003, 16% K002/K003/K004
C = 84% K002/K003, 16% K002/K003/K004
ND = Not detected.

Reference: USEPA 1987.

Table 4-2 (continued)

	Treated waste (lime flyash binder) TCLP sample number		
	A mg/l	B mg/l	C mg/l
Antimony	ND	ND	ND
Arsenic	ND	ND	ND
Barium	0.14	0.055	0.16
Beryllium	ND	ND	ND
Cadmium	ND	ND	ND
Chromium (Total)	45.4	4.5	ND
Copper	ND	ND	ND
Lead	6.3	14	73.4
Mercury	ND	ND	ND
Nickel	ND	ND	ND
Selenium	ND	ND	ND
Silver	ND	ND	ND
Thallium	ND	ND	ND
Vanadium	ND	ND	ND
Zinc	2.6	2.1	0.96

A = 84% K002/K003, 16% K002/K003/K004
B = 84% K003/K003, 16% K002/K003/K004
C = 84% K002/K003, 16% K002/K003/K004
ND = Not detected.

Reference: USEPA 1987.

Table 4-3 Stabilization Test Results for K006 Wastes Generated from Production of Chrome Oxide Green Pigment

Test number	TCLP extract total chromium (ppm)	TCLP extract hexavalent chromium (ppm)
1	0.95	0.53
2	0.26	<0.02
3	0.89	<0.02
4	4.25	0.33
5	1.08	0.23

Source: Pfizer Inc., 1989.

Effluent limitations Guidelines for the inorganic chemicals industry (USEPA 1982). These data show the results achievable using various methods for reduction of hexavalent chromium and precipitation of trivalent chromium and lead from wastewaters. The data also show the results of treatments for simple and complex cyanides.

5. IDENTIFICATION OF BEST DEMONSTRATED AVAILABLE TECHNOLOGY (BDAT)

This section presents the Agency's rationale for determining best demonstrated available technology (BDAT) for K002, K003, K004, K005, K006, K007, and K008 nonwastewaters and wastewaters. EPA notes, however, that this applies only to wastes from current management, and not to materials such as leachate, contaminated environmental media, or other residues derived from historic management of these wastes.

To determine BDAT, the Agency examines all available performance data on technologies that are identified as demonstrated to determine (using statistical techniques) whether one or more of the technologies performs significantly better than the others. The technology that performs best on a particular waste or waste treatability group is then evaluated to determine whether it is "available." To be available the technology must (1) be commercially available to any generator and (2) provide "substantial" treatment of the waste, as determined through evaluation of accuracy-adjusted data. In determining whether treatment is substantial, EPA may consider data on the performance of a waste similar to the waste in question provided that the similar waste is at least as difficult to treat. If the best technology is found to be not available, then the next best technology is evaluated, and so on.

The most desirable waste management technology is one that results in no residual streams or a residual stream with no hazardous properties. In this instance, product reuse/recycle eliminates the waste streams (K002, K003, and K006 from anhydrous chrome oxide green pigment production) entirely and is therefore the preferred management method, where applicable. However, the Agency notes that these technologies may not apply for all potential generators of these wastes. Of the three demonstrated technologies, HTMR, stabilization, and product reuse/

recycle, only the last has the potential to eliminate the waste stream entirely. Both HTMR and the use of chemical treatment and stabilization in series generate residuals. The HTMR residuals will contain much lower levels of toxic constituents than the listed waste. Chemical treatment followed by stabilization generates a residual that still requires land disposal and has not been reduced in volume or total mass of hazardous constituents.

Stabilization has been determined to be the most viable treatment method for K006 nonwastewaters originating from the facility producing hydrated chrome green pigment. The waste does not contain significant levels of lead or zinc, which could be recovered, and the levels of chromium present are far too low to make the material useful either as recycled material or as a feedstock to a process using chrome ore.

Stabilization has also been determined to be the most viable treatment technology for K002 and K003 nonwastewaters, based on the treatment of process wastewaters with lime and ferrous salts. Such wastes will contain relatively low levels of lead and will also contain high levels of calcium making them undesirable for high temperature treatment processes which might recover the lead.

At present, the one facility which sends its lead rich waste to a smelter does not use chromate reduction as part of its wastewater treatment train. As a result, this waste contains lead chromate. Tables 4-1 and 4-2 showed that this waste when stabilized with alkaline materials sometimes shows unacceptable chromium levels in TCLP leachates. The waste generated by the second facility is the result of a treatment process which reduces all hexavalent chromium compounds to trivalent chromium hydroxide. As a result, the waste from this second facility should behave like the sludges from K062 treatment which were the result of wastewater treatments that included chromium reduction.

Such K062 sludges when stabilized, passed the TCLP leachate test for chromium and lead as is evidenced by data presented in the K062 Background Document (USEPA 1988f). Also, stabilization has been determined by the Agency to be BDAT for the waste K046, wastewater treatment sludge from the production of lead based initiating compounds, which contains high levels of lead (USEPA 1988e).

The wastes K004 and K008 are expected to contain the same toxic constituents as the K002, K003 and K006 wastes. As a result, chemical treatment for chromate reduction followed by stabilization of the solids generated should also be applicable to these wastes.

The wastes K005 and K007 contain complex cyanides. K005 also contains chromates. Proven treatment to oxidize cyanides either by electrolytic oxidation or by alkaline chlorination are discussed in the treatment technology background document (USEPA 1988d) the F006 background document (USEPA 1988a) and the F007 background document (USEPA 1989). The Agency believes that these technologies are proven and applicable to K005 and K007 wastes because cyanides are present at comparable concentrations. Chromate reduction technology is also applicable to K005 wastes. Stabilization, as discussed in the F006 background document (USEPA 1988a) is applicable to all the chemically treated nonwastewater sludges thus created.

Treatment of wastewater forms of K002, K003, K004, K005, K006, K007, and K008 by chemical treatment and precipitation will convert wastewater forms of these wastes into much lower volumes of solid or semisolid forms of these materials. These residuals, however, are expected to be of highly variable composition.

6. SELECTION OF REGULATED CONSTITUENTS

6.1 Selection of Regulated Constituents for Nonwastewaters

The constituents of concern in nonwastewater form of K002 and K003 are lead and chromium. In Section 2.2 data on composition of these waste streams are presented which indicates that lead and chromium are the only BDAT list constituents present at significant levels in these wastes. Additional data, also in Section 2.2 show that chromium is the only BDAT list constituent present at treatable levels in nonwastewater forms of K004 and K006.

Data available from the original listing documents for the wastes K005, K007 and K008, which are not currently generated, indicate that chromium and cyanide are the constituents of concern in K005. Cyanide is the only constituent of concern in K007 and chromium is the sole constituent of concern in the waste K008.

As was discussed earlier in Sections 2.2 and 2.3, many plants produce more than one of the inorganic pigments and use or have used common wastewater treatment systems for management of wastewaters from these production operations. As a result, many of the nonwastewater forms of the wastes K002, K003, K004, K005, K006 (from anhydrous chrome oxide green production), K007 and K008 would be mixtures of these wastes. For this reason, the Agency is proposing that the constituents of concern for these wastes are chromium and lead. The Agency is also proposing cyanides as a regulated constituent for K005 and K007 wastes or waste mixtures, since they were listed for cyanides.

For K006 generated from the production of hydrated chrome oxide green only chromium is proposed as the constituent of concern. The sole production facility for this pigment has only produced this one pigment

in its history of operation and does not mix this production waste with the wastes from the manufacture of other pigments. Therefore, for this nonwastewater, chromium is the only constituent of concern.

6.2 Selection of Regulated Constituents for Wastewaters

In Sections 2 and 3 of this background document, the nature of the wastewater forms of K002, K003, K004, K005, K006, K007, and K008 were discussed. These wastewaters arise basically from two sources: leachates from landfills containing these wastes, and wastewaters arising from the treatment of one or more of these as generated nonwastewaters. These wastewaters have the potential, as a result, to contain all of the constituents of concern present in the nonwastewater forms of K002, K003, K004, K005, K006, K007,, and K008. For this reason, the Agency is proposing to regulate lead, chromium and total cyanide in these wastewaters, as it did for the nonwastewaters.

7. DEVELOPMENT OF BDAT TREATMENT STANDARDS

The Agency is proposing a treatment standard based on chemical treatment and subsequent stabilization in the case of the nonwastewater forms of K002, K003, K004, K005, K006 (from anhydrous chrome oxide green production), K007 and K008 and is transferring standards from the use of these technologies from the listed waste K062 which contains similar concentrations of lead and chromium. The specific treatment technologies involved are chromate reduction and lime and/or sulfide precipitation. For cyanides, the Agency is proposing use of alkaline chlorination of the wastes K005 and K007 as a means of destroying the cyanide present. The proposed BDAT treatment standards for K002, K003, K004, K005, K006 (from anhydrous chrome oxide green), K007 and K008 nonwasatewaters are as follows:

Constituent	TCLP Concentration in mg/l
Chromium (total)	0.094
Lead (total)	0.37
Cyanide	Alkaline chlorination of sludge or wastewater containing the sludge

In the case of K006 generated from the production of hydrated chrome oxide green pigment the Agency is proposing a standard based on stabilization and transferred from the use of this technology with the listed waste F006. This waste will contain boron compounds rendering it more difficult to stabilize and data supplied by the facility (see Table 4-3) indicates such a standard can be met. The proposed BDAT treatment standards for K006 from production of hydrated chrome oxide green are as follows:

Constituent	TCLP Concentration in mg/l
Chromium (total)	5.2
Chromium (hexavalent)	0.52

For the wastewater forms of K002, K003, K004, K005, K006, K007 and K008, the Agency is proposing the following treatment standards based on the Effluent Guidelines Limitations for the chrome pigments subcategory of the Inorganic Chemical Industry (USEPA 1982), because wastewater forms of these wastes should closely resemble the wastewaters generated by the inorganic pigments industry.

Constituent	Concentration in mg/l	
	30-day average	24-hour maximum
Chromium (total)	1.2	2.9
Lead (total)	1.4	3.4
Cyanide (total) for K005 and K007 only	0.31	0.74

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